ELECTROCHEMICAL OXIDATION OF Mn(II) TO MnO_4^- IN THE PRESENCE OF Ag(I) CATALYST

CH. COMNINELLIS* and J. PH. PETITPIERRE

Institute of Chemical Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

(Received 9 July 1990; in revised form 4 September 1990)

Abstract—It is confirmed that Ag(I) is a very effective catalyst for the oxidation of Mn(II) to permanganate. At anodic potentials below +1300 mV ($vs \text{ Hg}/\text{Hg}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ reference electrode) in 30% H₂SO₄ at 10°C, the current efficiency of permanganate formation is high; above 1300 mV AgO is deposited at the anode and the current efficiency of permanganate decreases due to the side reaction of oxygen evolution.

Key words: electrocatalysis, mediator, permanganate.

1. INTRODUCTION

It has been known for some time that Ag(I) is a good catalyst in the anodic oxidation of both inorganic and organic species[1]. More recently our group and several others have demonstrated that Ag(I) is a very effective mediator for the generation of redox reagents such as cobalt(III), manganese(III), cerium(IV) and dichromate[2–10], which are both strong and selective oxidizing agents for organic molecules.

The contribution of Boardman *et al.*[10] is particularly interesting because it shows the possibility of formation of permanganate in a sulphuric medium in the presence of Ag(I). The obtention of MnO_4^- by a relatively simple process is of evident interest in organic synthesis. The object of this work is to define more precisely the experimental conditions which allow the obtainment of permanganate with good current efficiency, and to try to understand better the mechanism of its formation.

2. EXPERIMENTAL

Preparative electrolysis was carried out in an electrolytic cell of 11 capacity. The anode was made of a platinum cylinder (90 cm² area) and the cathode was a platinum spiral enclosed in a porous porcelain pot; $Hg/Hg_2SO_4K_2SO_4$ (sat) was used as the reference electrode. All potentials in this paper are quoted against this electrode. Much detail on the electrochemical cell is given elsewhere[11].

The analysis of manganese at oxidation states higher than (II) (oxidant) are measured by iodometric titration. Two titrations had been done during electrolysis:

(a) Titration of the crude electrolyte (the sample was taken under stirring and contains soluble and insoluble oxidants); this gives the "total oxidant".

(b) Titration of the clear solution (obtained after centrifugation); this gives the "soluble oxidant".

The amount of MnO_2 formed was determined from these two titrations using the relation:

 $[MnO_2] = [total oxidant] - [soluble oxidant].$

The permangante was determined by uv ($\lambda_{max} = 522 \text{ nm}$; $E_{max} = 2370 \text{ I mol}^{-1} \text{ cm}^{-1}$) or/and by extraction with methylene chloride in the presence of tetrabutyl ammonium hydrogenosulphate and analysis by potentiometric titration[10].

The Mn(III) is calculated from the relation

 $[Mn(III)] = [soluble oxidant] - [MnO_4^-].$

3. RESULTS AND DISCUSSION

To demonstrate the catalytic effect of Ag(I) on the oxidation of Mn(II) a series of electrolyses was carried out on solutions of 50 mM Mn(II) in 30% sulphuric acid at 10°C in the absence and in the presence of Ag(I) (10 mM). Typical curves for the evolution of Mn(III), MnO₂ and MnO₄⁻ during electrolysis are shown in Fig. 1A for electrolysis carried out in the absence of Ag(I) and in Fig. 1B for electrolysis catalysed by Ag(I).

In the absence of Ag(I) only Mn(III) and MnO₂ are present during electrolysis (only a very small amount of MnO₄⁻ is formed after the passage of a large electrical charge). The Mn(III) concentration passes through a maximum then decreases due to its transformation to MnO₂.

In this case the following reaction scheme is proposed[12]

$$Mn(II) \rightarrow Mn(III) + e$$

$$Mn(III) + 2H_2O \rightarrow MnO_2 + 4H^+ + e.$$

In the presence of Ag(I) the situation is completely different, in particular MnO_2 is absent and a large

^{*}To whom correspondence should be addressed.



Fig. 1. Electrochemical oxidation of Mn(II): (a) in the absence of Ag(I); and (b) in the presence of Ag(I) (10 mM). Electrolyte: 50 mM Mn(II) in 30% H₂SO₄. T: 10°C; $i = 45 \text{ mA cm}^{-2}$. \bigcirc Mn(III); \bigcirc MnO₂; \bigcirc MnO₄.

amount of MnO_4^- is formed. In this case oxidation occurs via Ag(II) (or AgO):

$$Mn(II) + Ag(II) \rightarrow Mn(III) + Ag(I)$$

 $Mn(III) + 4Ag(II) + 4H_2O \rightarrow MnO_4^- + 8H^+ + 4Ag(I).$

To find the best conditions for the formation of permanganate a series of electrolysis was carried out under different conditions (temperature, H_2SO_4 concentration, current density) then the current efficiency for permanganate formation $(\eta_{MnO_4^-})$ and/or the Mn(II) to permanganate conversion $(X_{MnO_4^-})$ were determined.

Figure 2 shows the influence of temperature on $X_{MnO_{4}}$; at temperatures above 30°C the permanganate is not formed, contrary to low temperatures (10°C) where a high $X_{MnO_{4}}$ is observed ($\simeq 60\%$).

The absence of permanganate above 30° C is due to hydrolysis of Mn(III) to MnO₂:

$$2Mn(III) + 2H_2O \rightarrow MnO_2 + Mn(II) + 4H^+$$
.

The influence of H_2SO_4 concentration on X_{MnO_4} is shown in Fig. 3. A maximum of permanganate conversion is obtained in 30% H_2SO_4 . This maximum can be explained by the fact that the H_2SO_4 concentration has two opposite effects; at low concentrations the hydrolysis of Mn(III) is favoured and at high H_2SO_4 concentrations chemical decomposition of permanganate occurs.

The anode potential and consequently the current density strongly influence the current efficiency for permanganate formation; Table 1 shows that the electrolysis at an anodic potential above 1300 mV (critical anode potential) results in a rapid decrease in

100



Fig. 2. Influence of temperature on the conversion of Mn(II) to MnO_4^- (X_{MnOi}). Electrolyte: 50 mM Mn(II) + 10 mM Ag(I) in 30% H₂SO₄. T: 10°C, i = 45 mA cm⁻². Electrical charge passed: 18 electrons molecule⁻¹.

Fig. 3. Influence of H_2SO_4 concentration on the conversion of Mn(II) to MnO_4^- ($X_{MnO_4^-}$). Electrolyte: 50 mM Mn(II) + 10 mM Ag(I). T: 10°C, $i \approx 45$ mA cm⁻². Electrical charge passed: 25 electrons molecule⁻¹.

Table 1. Influence of current density and anode potential on the current efficiency of permanganate formation*

<i>i/</i>	5	10	20	30	45
	5	10	20	50	45
$ \begin{array}{c} E_a \\ mV \\ (\pm 30) \end{array} $	1200	1250	1300	1320	1370
n _{mnOi} / %:	67	59	26	24	24

*Electrolyte: 50 mM Mn(II), 10 mM Ag(I) in 30% H_2SO_4 . *T*: 10°C. Conversion of Mn(II) to $MnO_4^- - 75\%$.

current efficiency for permanganate formation. This phenomenon has been attributed to the deposition of AgO at the anode surface[11].

From these results, depending on the anode potential (E_a) , we can postulate two different mechanisms for the catalytic oxidation of Mn(II) to permanganate in the presence of Ag(I):

(i) For $E_a < 1300 \text{ mV}$ catalysis is due to oxidation of Mn(II) with Ag(II) formed at the anode:

$$5Ag(I) \rightarrow 5Ag(II) + 5e$$

 $Mn(II) + 4H_2O + 5Ag(II) \rightarrow MnO_4^- + 5Ag(I) + 8H^+.$

(ii) For $E_a > 1300 \text{ mV}$ the side reaction of water electrolysis increases strongly due to the anodic deposition of AgO which has high electrocatalytic properties for oxygen evolution:

$$2H_2O \xrightarrow{[AgO]} O_2 + 4H^+.$$

The formation of permanganate in this potential region is carried out by oxidation with AgO present at the anode surface:

$$5Ag(I) + 5H_2O \rightarrow 5AgO + 10H^+ + 5e$$

$$4$$

$$Mn(II) + 5H_2O + 5AgO \rightarrow MnO_4^- + 5Ag(I) + 10H^+.$$

Limitation by mass transfer rate of Mn(II)near the anodic surface can also contribute on the increasing side reaction of oxygen evolution.

To summarize, the best conditions for the formation of permanganate by the electrochemical oxidation of Mn(II) in the presence of Ag(I) catalysts are:

—using 30% H_2SO_4 as the electrolyte;

-use an anodic potential below 1300 mV (critical potential);

—low temperature ($\cong 10^{\circ}$ C).

REFERENCES

- 1. M. Fleischmann, D. Pletscher and A. Rafinski, J. appl. Electrochem. 1, 1 (1971).
- 2. C. Comninellis, E. Plattner and P. Javet, J. appl. Electrochem. 9, 595 (1979).
- 3. C. Comninellis, E. Plattner and P. Javet, J. appl. Electrochem. 9, 753 (1979).
- 4. C. Comninellis and E. Plattner, J. appl. Electrochem. 13, 117 (1983).
- 5. C. Comninellis and E. Plattner, J. electrochem. Soc. 129, 749 (1982).
- C. Griessen, Ph.D. thesis No. 576, Ecole Polytechnique Fédéral de Lausanne (1985).
- J. J. Jow and T. C. Chow, J. appl. Electrochem. 18, 298 (1988).
- 8. K. H. Oehr and T. Witcombe, Abstract No. 397 of the Electrochem. Soc. Meeting, Montreal (1982).
- 9. J. Lin-Cai and D. Pletcher, J. electroanal. Chem. 152, 157 (1983).
- D. W. Boardman, J. Lin-Cai and D. Pletcher, J. electroanal. Chem. 149, 49 (1983).
- 11. J. Ph. Petitpierre, Thèse No. 775 (1989) EPFL.
- 12. J. Ph. Petitpierre, Ch. Comninellis and E. Plattner, Electrochem. Acta 35, 281 (1990).